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Influence of high dose neutron irradiation on microstructure of EP-450 ferritic–martensitic steel irradiated in three Russian fast reactors

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Abstract

The microstructure of EP-450 ferritic–martensitic steel was determined after irradiation in BN-350, BN-600 and BR-10 fast reactors at temperatures in the range 275–690 °C. The examinations confirm a high resistance of EP-450 steel to void swelling, but the resistance appears to be lower when the dpa rate is reduced. Depending on irradiation dose and temperature the following was observed: voids (285–520 °C), dislocation loops and linear dislocations (275–520 °C), α'-phase (285–520 °C), χ-phase (460–590 °C), and M_2X precipitates (460–690 °C). It appears that the formation of dislocation loops and α' precipitates at high densities is responsible for the low temperature embrittlement observed in this steel.

1. Introduction

Ferritic/martensitic (F/M) steels are known for their high resistance to swelling and relatively low irradiation creep rate, and therefore are attractive as possible fusion candidate materials. The steel EP-450 is used most widely in Russia and CIS states, especially as the reference structural material of hexagonal wrappers and safety control tubes of the BN-600 fast reactor. An effort is underway to compile the microstructural data for this steel, with the main experimental database obtained by examination of hexagonal wrappers from the BN-350 and BN-600 fast reactors and of fuel pin cladding irradiated in BR-10 and BN-350 reactors. BR-10 and BN-600 have relatively high inlet temperatures compared to that of BN-350. BR-10 has the lowest neutron flux, producing $\sim 7\times 10^{-8}$ dpa/s, while the other two reactors operate at higher fluxes, producing $1–2\times 10^{-6}$ dpa/s. The first preliminary results are presented in this paper.

2. Experimental details

The compositions of all specimens examined fall within the limits of the EP-450 specification (0.1–0.15C, <0.8Mn, <0.5Si, 0.015S, <0.025P, 11.0–13.5Cr, 0.05–0.30Ni, 1.2–1.8Mo, 0.1–0.3V, 0.3–0.6Nb, wt%). The final heat treatment for hexagonal wrappers of BN-350 and BN-600 reactors sub-assemblies involves normalization at 1020–1100 °C with subsequent tempering at 780–800 °C for 1 h. For fuel pin cladding, however, normalization proceeds at 1050 °C followed by tempering at 710 °C for 1 h.

Sections of 15 mm length and 4 mm width were cut out from fuel cladding using a remote milling machine. Then disks of 3 mm in diameter were punched from the segments. For hexagonal wrappers (flat-to-flat distance of 96 mm and wall thickness of 2 mm) sections of size

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10×10 and 0.8–1.0 mm in thickness were cut from the middle of the faces. Following electrolytic thinning of the sections to a thickness of 0.4 mm, disks of 3 mm in diameter were punched. TEM specimens were prepared by a standard technique of two-jet polishing using the 'TENUPOLE' device with electrolyte of 5 vol.% $HClO_4 + 95$ vol.% H_3COOH. Microstructural investigations were carried out at an accelerating voltage of 100 kV using a JEM-100CX electron microscope equipped with a lateral goniometer.

3. Experimental results

3.1. Void structure

The initial microstructure was similar for both wrappers and tubes, consisting of grains of ferrite (40–50%) and tempered martensite (50–60%), with grain sizes of ferrite and martensite ranging 17–50 μm. Grains in tempered martensite were divided into sub-grains. The dislocation density was $\sim 2\times10^{14}$ m^{-2} in ferritic grains, and $\sim 110^{15}$ m^{-2} in martensite.

Both ferrite and martensite contain $M_{23}C_6$ carbides in the matrix and on grain boundaries. The grain boundary occupation by $M_{23}C_6$ was 90–100%, with particle sizes of 0.05–0.50 μm. Inside ferrite grains the carbide sizes ranged from 0.05 up to 0.2 μm, and their concentration in some grains reached 2×10^{20} m^{-3}. In the tempered martensite $M_{23}C_6$ precipitates were located, as a rule, on sub-grain boundaries, with mean sizes of 0.15–0.3 μm. Carbonitrides such as M (C, N) with mean size of ~ 1 micron were also observed inside ferrite and martensite grains. Additionally, small plate-like precipitates of M_2 (C, N) were observed in ferrite grains.

The microstructure of the steel changed significantly due to irradiation. Voids, dislocation loops and new precipitates have formed, with size and concentration depending on irradiation conditions. Parameters of voids observed to date and swelling S are shown in Table 1.

Isolated voids of 4 nm diameter formed after irradiation to 0.5 dpa at the temperature of 285 °C in BN-350. Further increases of dose resulted in an increase of void concentration. At irradiation temperatures in the

Table 1
Parameters of voids observed in neutron irradiated EP-450 F/M steel

Reactor	Sample type	Irradiation conditions		Voids		
		$T_{irr.}$, °C	dpa	d_v, nm	N_v, 10^{21} m^{-3}	S, %
BR-10	Fuel pin	360	9.7	–	0	0
BR-10	Fuel pin	395	11	18	0.28	0.1
BR-10	Fuel pin	410	10.8	24	0.12	0.1
BR-10	Fuel pin	430	9.0	–	0	0
BN-350	Fuel pin	285	0.5	4	Very low	∼0
BN-350	Fuel pin	285	3.0	4	Very low	∼0
BN-350	Fuel pin	285	10	4	4	0.01
BN-350	Fuel pin	285	21	4	7	0.02
BN-350	Fuel pin	355	37	8	2	0.08
BN-350	Fuel pin	420	46	18	0.7	0.3
BN-350	Fuel pin	315	34	5.5	0.7	0.01
BN-350	Fuel pin	380	56	12	1	0.1
BN-350	Fuel pin	460	60	7	0.3	0.006
BN-350	Fuel pin	595	39	0	0	0
BN-350	Fuel pin	690	17	0	0	0
BN-350	Wrapper	275	4.7	–	0	0
BN-350	Wrapper	275	18.8	3	5	0.003
BN-350	Wrapper	305	33.5	5	4	0.015
BN-350	Wrapper	415	47	12	2	0.2
BN-350	Wrapper	520	18.8	14	0.1	0.01
BN-350	Wrapper	280	15	3	2.5	0.005
BN-350	Wrapper	352	89	13.5	3	0.6
BN-600	Wrapper	345	31	13	1	0.1
BN-600	Wrapper	360	<1	4	1	0.003
BN-600	Wrapper	365	42	10	0.4	0.03
BN-600	Wrapper	360	35	8	0.4	0.02
BN-600	Wrapper	365	39	8.5	0.4	0.02
BN-600	Wrapper	465	81	–	0	0

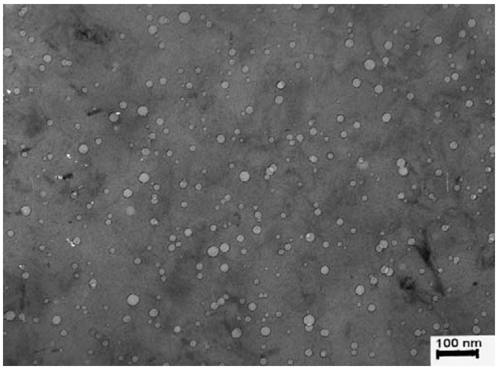

Fig. 1. Voids in EP-450 after irradiation as the structural material of hexagonal wrappers in BN-350 to 89 dpa at 352 °C.

285–460 °C range voids are uniformly distributed with no essential difference between grains of ferrite and tempered martensite (Fig. 1). For higher irradiation temperatures the spatial distribution of voids is non-uniform. Generally, voids in ferrite grains are adjacent to precipitates. In grains of tempered martensite they are located mainly on sub-grain boundaries. Voids were not observed at irradiation temperatures above 520 °C for the dose range available.

The average swelling rate for the specimens listed in Table 1 is shown in Fig. 2. The maximum average swelling rate is $\sim 1 \times 10^{-2}$%/dpa in the temperature range 390–410 °C. Note that the highest rate is observed at rather low dpa levels in BR-10, rather than at much higher dpa levels reached in BN-350. Remember that BR-10 operates at a much lower dpa rate.

3.2. Dislocation structure

Irradiation at temperatures from 275 to 520 °C results in formation of dislocation loops as shown in Fig. 3. For the space limitation of these proceedings it is not possible to list all dislocation data for the many specimens used in this study. These data will be published separately but we can specify the general observations.

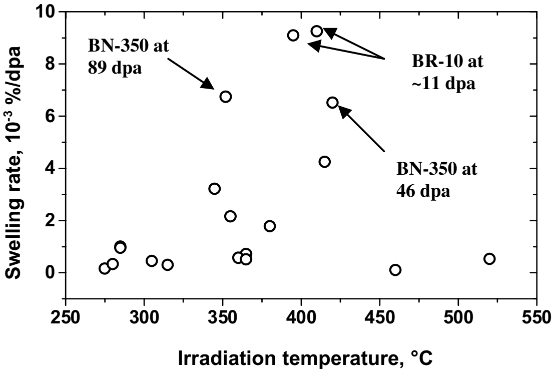

Fig. 2. Temperature dependence of the average swelling rate observed in EP-450.

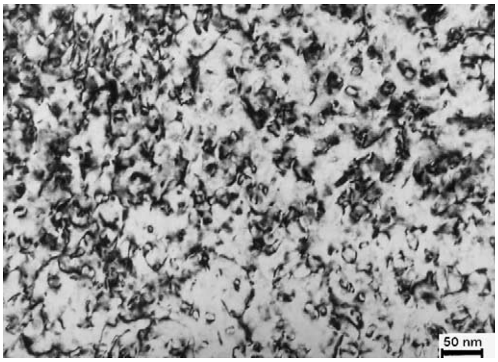

Fig. 3. Dislocation structure in ferrite grains of neutron irradiated EP-450 after irradiation in BN-600 to <1 dpa at 360 °C.

In ferrite grains both the mean loop diameter and loop concentration are slightly larger than in grains of tempered martensite. The mean loop diameter increases with increasing irradiation temperature. The loop concentration depends on both the temperature and dose. However, the influence of irradiation temperature appears to be more pronounced. Along with dislocation loops, radiation defects in the form of black dots are observed in the steel microstructure at the irradiation temperatures of 275 and 285 °C and doses <20 dpa. The dot number density is on the level of $\sim 10^{21}$ m^{-3} in both ferrite and tempered martensite grains.

In the range 360–520 °C dislocation loops interact with each other, as well as with any existing dislocation network. As a result of such interaction, the total dislocation density decreases with increasing temperature. The dislocation structure formed after irradiation at >520 °C consists of a dislocation network, the density of which is slightly higher in tempered martensite grains.

3.3. Precipitate structure

Formation of new precipitates as well as the transformation of pre-existing precipitates occurs in EP-450 under irradiation. At irradiation temperatures ranging from 275 to 520 °C a high concentration (10^{22}–10^{23} m^{-3}) of fine precipitates is observed in both the ferrite and tempered martensite (Fig. 4). These precipitates are α'-phase (ferrite enriched with chromium) usually formed in this type of steels under neutron irradiation [1–3]. After irradiation to only 3 dpa α' precipitates can be detected as strongly diffuse dots of 5 nm size.

An increase of irradiation temperature causes increased size of α' precipitates accompanied with simultaneous reduction of concentration. Uniform

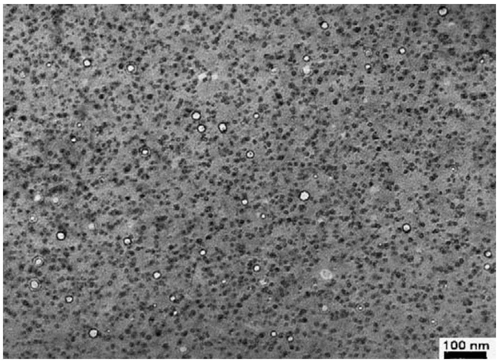

Fig. 4. α′-phase precipitates and voids observed in EP-450 irradiated in BN-350 reactor to 56 dpa at 380 °C.

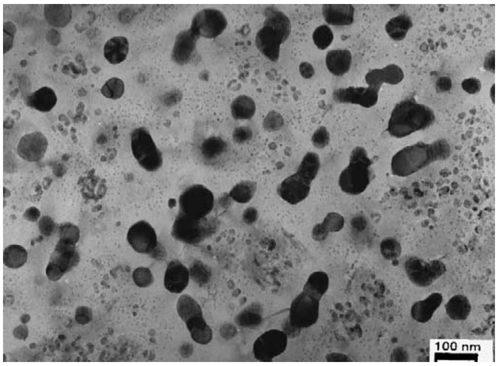

Fig. 5. Precipitates of χ-phase in EP-450 irradiated in BN-600 reactor to 81 dpa at 465 °C.

distribution of these particles is a characteristic feature at temperatures in the range of 275–480 °C. At 520 °C α′ precipitates are observed as islands of small clusters, with concentration 1×10^{21} m^{-3} and mean diameter of 16 nm. In addition, two types of radiation-induced precipitates were observed in ferrite grains, equiaxed precipitates of χ-phase (Fig. 5) and rod-like precipitates of M_2X (Fig. 6).

χ-phase formed in the range 460–590 °C, their size ranging from 35 to 60 nm with increasing temperature. Their concentration was largest at 515 °C and 55 dpa, with concentration of 5×10^{20} m^{-3}. M_2X particles formed in the 460–690 °C range, with size increasing from 80 to 600 nm with increasing temperature from 460 up to 690 °C, but with concentration maintained at $\sim5\times10^{19}$ m^{-3}.

Irradiation at 510–690 °C caused growth of $M_{23}C_6$ on grain boundaries and an increase of the occupation factor of sub-grain boundaries by carbides in tempered martensite grains, with the trend increasing with temperature. After irradiation at 690 °C blocky precipitates of $M_{23}C_6$ carbides of 100–500 nm in size were observed in ferrite grains. In tempered martensite grains new precipitates did not form, however.

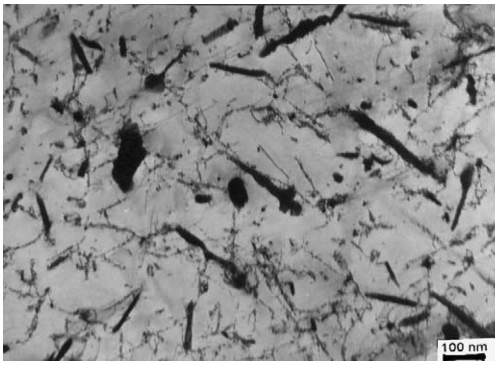

Fig. 6. M_2X precipitates observed in EP-450 irradiated in BN-350 reactor to 17 dpa at 690 °C.

4. Discussion

Microscopy has confirmed the relatively low susceptibility of the EP-450 steel for neutron-induced swelling in fast reactors. Voids were found in the 275–520 °C temperature range, but the maximum swelling level at doses to 90 dpa did not exceed 1%.

The maximum average swelling rate of $\sim1\times10^{-2}$%/dpa was observed at 395–410 °C, but it must be noted that this average is calculated over the entire dose, including that portion associated with the incubation-transition regime. Nevertheless, this maximum rate is much lower than the 2×10^{-1}%/dpa maximum swelling rate predicted by Garner and co-workers for ferritic/martensitic steels [4,5]. It is of interest to note, however, that swelling rate of $\sim1\times10^{-2}$%/dpa was observed after irradiation in BR-10 at a rather low displacements rate of 7.6×10^{-8} dpa/s. For comparison, the dose rate in BN-350 and BN-600 is $\sim(1–2)\times10^{-6}$ dpa/s. Garner and co-workers have predicted that ferritic/martensitic alloys will swell more at lower dpa rates due to a flux-dependent shortening of the transient regime of swelling [4]. They have also explored the competing effects of different He/dpa ratios and dpa rates to influence the duration of the transient regime [6], but in the case of these three fast reactors there are not large differences in neutron spectra and resulting He/dpa ratio.

Previous measurements of mechanical properties of the EP-450 steel have shown that both pin cladding [7] and hexagonal wrappers [8] experience low-temperature irradiation embrittlement. Based on the observations in this paper it appears that the combined effect of dislocation loops and α′ precipitates produces the embrittlement of EP-450 steel, especially at lower temperatures where their density is highest. The α′-phase, in particular, is known to be responsible for embrittlement during aging and irradiation of chromium steels [9,10]. It has been particularly established, that the formation of α' is responsible for deterioration of impact properties of ferritic steels [11].

5. Conclusions

The microstructure of ferritic/martensitic EP-450 steel has been studied after irradiation in three Russian fast reactors when serving as the structural material of hexagonal wrappers and fuel pin cladding at temperatures in the range of 275–690 °C up to maximum dose of 89 dpa. It is shown that radiation-induced microstructural evolution proceeds in a manner which is dependent on irradiation temperature, dpa level and possibly dpa rate. The influence of dpa rate on swelling is of particular interest, leading to earlier and larger levels of void swelling at lower dpa rates, in agreement with the results and predictions of earlier studies. Radiation-induced modification of phase stability was also observed and appears to be strongly related to irradiation temperature.

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